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Supercritical Drying Method and Apparatus

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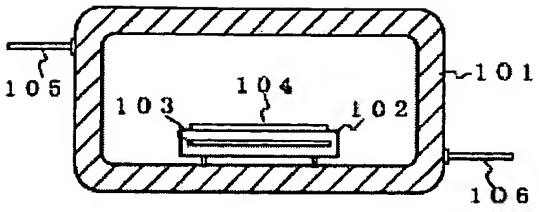
(54) [Title of the Invention] Supercritical Drying Method and Apparatus

(57) [Summary]

[Object] To provide an arrangement whereby supercritical drying can be performed more rapidly as a result of removing the rinsing solution remaining on a pattern in a shorter time.

[Means of Achievement] A substrate 104 contaminated with a rinsing solution is fixed in place on a substrate holder 102, the pressure chamber 101 is hermetically sealed, liquefied carbon dioxide is pumped through an inlet 105, and the interior of the pressure chamber 101 is filled with the liquefied carbon dioxide. Once the liquefied carbon dioxide is introduced into the pressure chamber 101 and the substrate 104 is soaked in the liquefied carbon dioxide, electric power is supplied to ultrasonic generation means 103 and ultrasonic waves are generated.



[Claims]

[Claim 1] A supercritical drying method, characterized in comprising:

a first step in which a patterned layer obtained by means of forming a specific pattern on a substrate is exposed to the action of a rinsing solution;

a second step in which, with the rinsing solution deposited on the patterned layer, the substrate is placed in a container, a liquid substance that is a gas at atmospheric pressure is introduced into the container, and conditions are created in which the patterned layer is exposed to the action of the liquid substance;

a third step in which ultrasonic waves are applied to the liquid from an ultrasonic generator located inside the container at a distance from the inner walls of the container, and the rinsing solution deposited on the patterned layer is removed;

a fourth step in which the liquid substance introduced into the container is converted to a supercritical fluid in a supercritical state, and the patterned layer is exposed to the action of the supercritical fluid; and

a fifth step in which the supercritical fluid inside the container is discharged from the container to lower the pressure inside the container, to gasify the supercritical fluid, and to expose the patterned layer to the action of the gas.

[Claim 2] A supercritical drying apparatus, characterized in comprising:

a sealable container for accommodating a substrate workpiece in the interior thereof;

liquid feeding means for feeding a liquid substance that is a gas at atmospheric pressure into the container;

discharge means for discharging the fluid introduced into the reaction chamber[1];

control means for controllably raising the pressure inside the reaction chamber to the pressure at which a supercritical state is established;

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[1] Translator's note: There is no previous reference to a "reaction chamber" in the document.

temperature control means for controllably keeping the temperature inside the reaction chamber at a specific level; and

ultrasonic generation means that is located inside the container at a distance from the inner walls of the contained and is provided with an ultrasonic generator for applying ultrasonic waves inside the container.

[Claim 3] The supercritical drying apparatus according to claim 2, characterized in that the ultrasonic generator is held in a substrate holder for holding the substrate inside the container.

[Claim 4] The supercritical drying apparatus according to claim 2, characterized in that the ultrasonic generation means is composed of the ultrasonic generator, which itself comprises an oscillator located outside the container, and a resonator that is caused to resonate to the vibrations from the oscillator and to generate ultrasonic vibrations.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a supercritical drying method for forming fine patterns in the production of semiconductor devices, and, more particularly, to a supercritical drying method and apparatus used in forming fine patterns by means of lithography.

[0002]

[Prior Art] Fine patterns need to be formed in order to manufacture LSI circuits and other large/high-performance devices. Such patterns are primarily formed by means of lithographic techniques, in which exposure, development, and rinsing are employed to create resist patterns. Resist patterns formed with the help of such lithographic techniques are composed of polymer materials sensitized to light, X rays, electron beams, and the like. There are also etching techniques, which involve etching, washing, and rinsing.

[0003] However, forming ultrafine patterns with the help of such patterning techniques is disadvantageous in that the patterns sometimes collapse, making it impossible to form patterns capable of meeting the intended targets. The pattern collapse phenomenon occurs in the following manner: a resist pattern 602 formed on a substrate 601 is immersed in a rinsing solution 603, and the rinsing solution is then removed, as shown in Fig. 6(a). At this stage, the rinsing solution 603a remains between the elements of the resist pattern 602, which are located

adjacent to each other at a fine pitch, as shown in Fig. 6(b). When such a state is established, the capillary force 610 of the rinsing solution 603a acts on the pattern 602, and the pattern 602 collapses after the rinsing solution 603a has been completely removed, as shown in Fig. 6(c).

[0004] The capillary force 610 is created as a result of the difference between the atmospheric pressure and the pressure inside the rinsing solution 603a remaining between the pattern elements located at a narrow pitch, and this force is related to the surface tension of the rinsing solution 603a. Consequently, the capillary force increases and the pattern is more likely to collapse with an increase in the surface tension of the rinsing solution. A rinsing solution of low surface tension should be used to perform the rinsing treatment in order to prevent patterns from being collapsed as a result of the capillary force.

[0005] Surface tension is generated when an interface forms between a liquid and a gas. Consequently, pattern collapse can be reduced if rinsing is performed while an interface is prevented from forming between a liquid and a gas. Methods that employ supercritical liquids may be used to perform rinsing without forming an interface between a liquid and a gas. According to these methods, the rinsing solution is replaced with a supercritical liquid after the pattern is immersed in the solution, and the supercritical liquid is gasified in a state in which the only medium in contact with the pattern is the supercritical liquid.

[0006] A supercritical liquid has both the dispersibility of a gas and the solubility (high density) of a liquid, and changes its state to gas without passing through the equilibrium line. For this reason, drying a pattern in a container filled with a supercritical liquid in the above-described manner will make it possible to perform the drying process without forming a liquid/gas interface that generates surface tension during drying, and will therefore prevent such surface tension from being generated. As a result, pattern collapse can be suppressed in a drying process (rinsing treatment) performed using a supercritical liquid.

[0007] Carbon dioxide and other safe substances that are nonflammable and have a low critical point (supercritical point) are commonly used as such supercritical liquids. In addition, a supercritical drying apparatus in which a substrate holder 702 for supporting a substrate workpiece 704 is located inside a pressure chamber 701 capable of withstanding high pressure, as shown in Fig. 7, is used for supercritical drying. The apparatus comprises an inlet 705 for introducing liquefied carbon dioxide, and an outlet 706 for discharging the fluid from the apparatus.

[0008] In a supercritical drying operation performed using such a supercritical drying apparatus, a resist pattern formed on a substrate 704 is first immersed in a rinsing solution, the substrate 704 is then fixed in place on the substrate holder 702, and the pressure chamber 701 is hermetically sealed. Liquefied carbon dioxide is introduced into the pressure chamber 701 while the rinsing solution on the substrate 704 has not yet dried, the rinsing solution is allowed to mix with the liquefied carbon dioxide thus introduced, and the rinsing solution deposited on the resist pattern is replaced with the liquefied carbon dioxide. Carbon dioxide liquefies even at normal temperature if the pressure is raised to about 6 MPa, so the pressure inside the pressure chamber 701 must be raised to this level.

[0009] After the interior of the pressure chamber 701 has been filled with liquefied carbon dioxide and the substrate 704 has been completely covered with the liquefied carbon dioxide, the pressure and temperature inside the pressure chamber 701 are brought to the levels at which the liquefied carbon dioxide is in a supercritical state, and a condition is established in which the interior of the pressure chamber 701 is filled with carbon dioxide in a supercritical state. The introduction of liquefied carbon dioxide through the inlet 705 is then stopped, and the fluid inside is continuously released through the outlet 706, whereby the pressure inside the pressure chamber 701 is reduced, the supercritical carbon dioxide inside is gasified, and the resist pattern is dried. At this time, the supercritical carbon dioxide is gasified without being liquefied on the surface of the resist pattern, thus preventing surface tension from being generated, and the pattern from collapsing.

[0010] It is important that the rinsing solution deposited on the surface of the resist pattern as a result of the rinsing treatment be completely substituted with the liquefied carbon dioxide in order to prevent the pattern from being collapsed as a result of the supercritical drying operation. However, carbon dioxide, which lacks a dipole moment, has essentially the same low dissolution characteristics as does a hydrocarbon-based solvent, and is therefore poorly miscible with the alcohols or water commonly used for the rinsing solution. For this reason, introducing liquefied carbon dioxide to achieve substitution is a time-consuming process. This shortcoming can be overcome by means of using a technique in which a vibrating plate for generating ultrasonic waves is attached outside the pressure chamber to make it easier for the rinsing solution and the liquefied carbon dioxide to be mixed inside the pressure chamber, as described in JP (Kokai) 11-87306.

[0011]

[Problems to Be Solved by the Invention] This technique, however, is aimed at applying ultrasonic waves through the walls of the pressure chamber, and is therefore unsuccessful in making it appreciably easier for the rinsing solution and liquefied carbon dioxide to mix inside the pressure chamber, or in significantly shortening the substitution time. The present invention is aimed at overcoming this shortcoming and ensuring that supercritical drying can be performed rapidly as a result of removing the rinsing solution remaining on the pattern in a shorter time.

[0012]

[Means Used to Solve the Above-Mentioned Problems] The supercritical drying method in accordance with an embodiment of the present invention comprises a first step in which a patterned layer obtained by means of forming a specific pattern on a substrate is exposed to the action of a rinsing solution; a second step in which, with the rinsing solution deposited on the patterned layer, the substrate is placed in a container, a liquid substance that is a gas at atmospheric pressure is introduced into the container, and conditions are created in which the patterned layer is exposed to the action of the liquid substance; a third step in which ultrasonic waves are applied to the liquid from an ultrasonic generator located inside the container at a distance from the inner walls of the container, and the rinsing solution deposited on the patterned layer is removed; a fourth step in which the liquid substance introduced into the container is converted to a supercritical fluid in a supercritical state, and the patterned layer is exposed to the action of the supercritical fluid; and a fifth step in which the supercritical fluid inside the container is discharged from the container to lower the pressure inside the container, to gasify the supercritical fluid, and to expose the patterned layer to the action of the gas. With this supercritical drying method, the rinsing solution and a liquid substance that is a gas at atmospheric pressure are emulsified as a result of the application of ultrasonic waves.

[0013] The supercritical drying apparatus in accordance with an embodiment of the present invention comprises a sealable container for accommodating a substrate workpiece in the interior thereof; liquid feeding means for feeding a liquid substance that is a gas at atmospheric pressure into the container; discharge means for discharging the fluid introduced into the reaction chamber; control means for controllably raising the pressure inside the reaction chamber to the pressure at which a supercritical state is established; temperature control means for controllably keeping the temperature inside the reaction chamber at a specific level; and ultrasonic generation

means that is located inside the container at a distance from the inner walls of the contained and is provided with an ultrasonic generator for applying ultrasonic waves inside the container. With this supercritical drying apparatus, ultrasonic waves can be applied from the ultrasonic generator without the intervening container to the liquid introduced into the container.

[0014] In the supercritical drying apparatus as described in the foregoing, the ultrasonic generator may, for example, be held in a substrate holder for holding the substrate inside the container. Also, the ultrasonic generation means is composed of an ultrasonic generator that comprises an oscillator located outside the container, and a resonator that is caused to resonate to the vibrations from the oscillator and to generate ultrasonic vibrations.

[0015]

[Embodiments of the Invention] Embodiments of the present invention will now be described with reference to the drawings. Fig. 1 is a schematic cross section depicting the structure of a supercritical drying apparatus in accordance with an embodiment of the present invention. The supercritical drying apparatus may, for example, comprise a sealable pressure chamber (container) 101 capable of accommodating a supercritical liquid (about 10 MPa) in the interior thereof, and an ultrasonic generator means 103 is held in a substrate holder 102 fixedly mounted inside the pressure chamber 101. The ultrasonic generator means 103 comprises an ultrasonic oscillator and a vibrating plate (ultrasonic generator).

[0016] In the ultrasonic generator means 103, the vibrating plate is affixed as a resonator to the oscillator, which is an electromechanical transducer in which vibrations are induced as a result of the application of an electric signal, and wide-amplitude ultrasonic vibrations are generated using the resonance action of the resonator. The vibrating plate of the ultrasonic generator means 103 is caused to generate ultrasonic waves by means of supplying electric power to the ultrasonic oscillator and causing it to generate ultrasonic vibrations, and the ultrasonic waves thus generated are transmitted to the pressure chamber 101.

[0017] The supercritical drying apparatus comprises an inlet 105 for introducing liquefied carbon dioxide or another liquid substance that is a gas at atmospheric pressure, and also comprises an apparatus (not shown) connected to the inlet 105 and designed to pump in the aforementioned liquid, or a cylinder or other liquid feeding means for accommodating the liquid. The supercritical drying apparatus further comprises an outlet (discharge means) 106 for discharging the liquid from the pressure chamber 101. The outlet 106 is provided with a control valve or

other device (not shown) for controlling the discharge rate, and is configured to allow the pressure inside the pressure chamber 101 to be controlled.

[0018] Following is a description of the supercritical drying method performed using the supercritical drying apparatus of Fig. 1. A substrate 104 contaminated with a rinsing solution is fixed in place on the substrate holder 102, the pressure chamber 101 is hermetically sealed, liquefied carbon dioxide is pumped through the inlet 105, and the interior of the pressure chamber 101 is filled with the liquefied carbon dioxide. Once the liquefied carbon dioxide is introduced into the pressure chamber 101 and the substrate 104 is soaked in the liquefied carbon dioxide, electric power is supplied to ultrasonic generation means 103, and ultrasonic waves are generated.

[0019] The rinsing solution adhered to the pattern (patterned layer) on the substrate 104 is thereby allowed to rapidly mix with the liquefied carbon dioxide, and the replacement of the rinsing solution deposited on the pattern with the liquefied carbon dioxide can be completed in a short time. Following substitution, the liquefied carbon dioxide inside the pressure chamber 101 is brought to a supercritical state as a result of setting the pressure inside the pressure chamber 101 to 7.5 MPa, and the temperature to 31°C or greater, for example. At this time, the atmosphere around the pattern on the substrate 104 is composed solely of supercritical carbon dioxide.

[0020] After the carbon dioxide inside the pressure chamber 101 has been brought to a supercritical state, the introduction of liquefied carbon dioxide through the inlet 105 is stopped and the contained fluid is released through the outlet 106, whereby the pressure inside the pressure chamber 101 is reduced and the supercritical carbon dioxide is gasified. At this time, the supercritical carbon dioxide is gasified without being liquefied, thus preventing surface tension from being generated. As a result, the pattern on the substrate 104 is dried without being collapsed.

[0021] Following is a description of the action whereby the mixing of the rinsing solution and liquefied carbon dioxide is promoted as a result of the application of ultrasonic waves. First, a cavitation phenomenon occurs in a state in which a rinsing solution 203 adheres to a pattern 202 on a substrate 201, and the pattern 202 is bathed in liquefied carbon dioxide 204, when ultrasonic waves in the kilohertz band are applied in the vicinity thereof, as shown in Fig. 2(a). The cavitation phenomenon is one in which bubbles are produced in the period of negative pressure

during an acoustic pressure cycle of a sound wave in a liquid, and the bubbles thus produced are then collapsed in the period of positive pressure. When the bubbles are collapsed, the resulting shock wave produces pressure variations. Applying ultrasonic waves in the megahertz range reduces the cavitation phenomenon and creates a rectilinear flow. The effect of the rectilinear flow is to produce a stirring action on the liquefied carbon dioxide inside the pressure chamber 101.

[0022] The rinsing solution 203 deposited on the pattern 202 is thereby dispersed in the surrounding liquefied carbon dioxide 204, and the surrounding liquefied carbon dioxide 204 is dispersed in the rinsing solution 203, as shown in Fig. 2(b). In other words, the two substances disperse in each other, and emulsification of the liquefied carbon dioxide 204 and the rinsing solution 203 occurs as a result. The emulsification of the rinsing solution 203 and the liquefied carbon dioxide 204 results in the removal of the rinsing solution 203 from the surface of the pattern 202, and brings about conditions in which the periphery of the pattern 202 is covered with the liquefied carbon dioxide 204, as shown in Fig. 2(c). The liquefied carbon dioxide is subsequently brought to a supercritical state as described in the foregoing, and the pattern can be dried without being collapsed if the carbon dioxide is gasified.

[0023] In conventional practice, an ultrasonic generator is fixed in place on the external surface of a pressure chamber formed to a thickness (several centimeters or the like) designed to withstand a high pressure (10 MPa), making it impossible to provide the liquid in the chamber with an adequate ultrasonic output. For this reason, it was impossible in conventional practice to make it noticeably easier for the rinsing solution and the liquefied carbon dioxide to mix in the pressure chamber, or to adequately reduce the replacement time even when ultrasonic waves were used. Another feature of the conventional practice is that because the ultrasonic generator (vibrating plate) is attached directly to the pressure chamber, there are cases in which the pressure chamber itself resonates, the joints in the piping for introducing and discharging the high-pressure liquid become loose, and the liquid leaks or otherwise escapes.

[0024] In contrast to the prior art, the present embodiment entails placing the ultrasonic generator inside the pressure chamber at a distance from the inner walls thereof, making it possible to apply ultrasonic waves to the liquefied carbon dioxide (liquid substance that is a gas at atmospheric pressure) inside the pressure chamber with high efficiency and to efficiently replace the rinsing solution. In addition, the pressure chamber does not resonate, and the joints

in the piping for introducing and discharging the high-pressure liquid do not become loosened or the like.

[0025] The frequency of the ultrasonic waves falls within the commonly used range of 20 to 1,500 kHz. Within this range, the frequencies of 20 to 50 kHz are known to constitute a frequency range that is apt to produce the cavitation phenomenon. Consequently, the range of 20 to 50 kHz is the most effective range for the ultrasonic waves generated by the ultrasonic generator means 103. Stirring as a result of a rectilinear flow begins to predominate at higher frequencies (when, for example, a so-called megasonic frequency of about 1 MHz is established), as described in the foregoing, causing the replacement efficiency to decrease in comparison with stirring by means of cavitation. However, the resonance thickness can be reduced by the use of such high frequencies, and, as a result, a thinner layer can be formed in the bottom area of ultrasonic generation, which is more advantageous for fitting the ultrasonic generator inside a thin pressure chamber.

[0026] It should also be noted that the structure in which the ultrasonic generator means 103 is mounted in the substrate holder 102 in the manner shown in Fig. 1 does not need to be configured such that the substrate holder 102 can withstand high internal pressure. Consequently, there is no need for the substrate holder 102 to be provided with considerable wall thickness in the manner adopted for the pressure chamber 101, the distance from the ultrasonic generator means 103 to the surface of the substrate holder 102 can be reduced, and the ultrasonic waves generated as a result of the ultrasonic generator means 103 can be applied with high efficiency to the liquid around the substrate holder 102.

[0027] In cases in which the ultrasonic generator means 103 in the substrate holder 102 is not monolithic but forms a space, the gap formed with the help of the ultrasonic generator means 103 inside the substrate holder 102 should be filled with resin 301, as shown in Fig. 3. Adopting this arrangement makes it possible to suppress any deformation in the substrate holder 102 brought about as a result of the high pressure inside the pressure chamber 101.

[0028] In addition, it is not necessary to place the entire ultrasonic generator means 103 in the substrate holder 102, and it is possible to adopt an arrangement in which only part of the vibrating plate (ultrasonic generator) as a component of the ultrasonic generator means 103 is located in the pressure chamber 101. For example, the ultrasonic generator means 103 can be located in the pressure chamber 101 above the substrate holder 102, as shown in Fig. 4.

Alternatively, an oscillator 103a is located outside the pressure chamber 101, a portion (ultrasonic generator) of the vibrating plate 103b that resonates to the vibrations generated with the help of the oscillator 103a is extended into the pressure chamber 101, and a substrate 104 is mounted thereon. In this case, the portion of the vibrating plate 103b that extends into the pressure chamber 101 and carries the substrate 104 serves as an ultrasonic generator.

[0029] The resonator need not have a tabular shape similar to that of the vibrating plate, and any structure or mode (including bar-shaped) may be adopted as long as it can resonate to the vibrations generated with the help of the oscillator. In addition, any resonator can be located in the pressure chamber 101 as long as this resonator can resonate to the vibrations of the oscillator and produce ultrasonic waves. For example, the resonator can be located beside the substrate holder 102. In any of these arrangements, the ultrasonic generator should be located inside the pressure chamber at a distance from the inner walls of the chamber.

[0030]

[Working Examples] A detailed description will now be given based on working examples.

<Working Example 1> ZEP-7000 (manufactured by Zeon Corp.), an electron-beam resist, was first spin-coated on a silicon substrate to form a resist film with a thickness of 250 nm. The resist film thus formed was subsequently exposed to electron beams to form the desired latent image, and the image was then developed with *n*-hexyl acetate and rinsed with 2-propanol (rinsing solution) to form a resist pattern on the silicon substrate. The resulting pattern had a width of 20 to 100 nm.

[0031] The silicon substrate (substrate 104) was then mounted on the substrate holder 102 in the pressure chamber 101 within the time frame during which the resist pattern could be kept wetted with the rinsing solution, the pressure chamber 101 was hermetically sealed, liquefied carbon dioxide was then pumped into the pressure chamber 101 through the inlet 105 at 100 mL/min while the outlet 106 was kept closed, and the pressure chamber 101 was filled with the liquefied carbon dioxide. In the process, the temperature of the pressure chamber 101 was kept at 23°C by means of a control from a container temperature controller (not shown).

[0032] Ultrasonic waves were generated with the help of the ultrasonic generator means 103 at the same time as the pressure chamber 101 was filled with liquefied carbon dioxide, and the rinsing solution deposited on the resist pattern was mixed with the liquefied carbon dioxide thus

introduced. In the process, the liquefied carbon dioxide was continuously introduced into the pressure chamber 101 under specific pumping conditions in a state in which the degree of opening of the outlet 106 was controlled, and the pressure inside the pressure chamber 101 was controlled so as to remain at 7.5 MPa. After the ultrasonic waves had been generated for 5 minutes, the temperature inside the pressure chamber 101 was raised to 35°C while the pressure inside the pressure chamber 101 was maintained at 7.5 MPa, and the liquefied carbon dioxide in the pressure chamber 101 was brought to a supercritical state.

[0033] The inlet 105 was then closed, the supply of the liquefied carbon dioxide was stopped, a condition was established in which the carbon dioxide alone was discharged through the outlet 106, and the interior of the pressure chamber 101 was brought to atmospheric pressure. This caused gasification of the supercritical carbon dioxide on the silicon substrate that carried the substrate holder 102, and brought about a state in which supercritical drying occurred. The resist pattern on the silicon substrate obtained as a result of such supercritical drying was free from pattern collapse and had an adequate pattern shape.

[0034] <**Working Example 2**> Working Example 2 will be described next. NEB-31, an electron-beam resist, was first spin-coated on a silicon substrate to form a resist film with a thickness of 250 nm. The resist film thus formed was subsequently exposed to electron beams to form the desired latent image, and the image was then developed with an aqueous solution of tetramethylammonium hydroxide and rinsed with purified water (rinsing solution) to form a resist pattern on the silicon substrate. The resulting pattern had a width of 20 to 100 nm.

[0035] The silicon substrate (substrate 104) was then mounted on the substrate holder 102 in the pressure chamber 101 within the time frame during which the resist pattern could be kept wetted with the rinsing solution, the pressure chamber 101 was hermetically sealed, liquefied carbon dioxide was then pumped into the pressure chamber 101 through the inlet 105 at 100 mL/min while the outlet 106 was kept closed, and the pressure chamber 101 was filled with the liquefied carbon dioxide. In the process, the temperature of the pressure chamber 101 was kept at 23°C by means of a control from a container temperature controller (not shown).

[0036] Ultrasonic waves were generated with the help of the ultrasonic generator means 103 at the same time as the pressure chamber 101 was filled with liquefied carbon dioxide, and the rinsing solution deposited on the resist pattern was mixed with the liquefied carbon dioxide thus introduced. In the process, the liquefied carbon dioxide was continuously introduced into the

pressure chamber 101 under specific pumping conditions in a state in which the degree of opening of the outlet 106 was controlled, and the pressure inside the pressure chamber 101 was controlled so as to remain at 7.5 MPa. After the ultrasonic waves had been generated for 5 minutes, the temperature inside the pressure chamber 101 was raised to 35°C while the pressure inside the pressure chamber 101 was maintained at 7.5 MPa, and the liquefied carbon dioxide in the pressure chamber 101 was brought to a supercritical state.

[0037] The inlet 105 was then closed, the supply of the liquefied carbon dioxide was stopped, a condition was established in which the carbon dioxide alone was discharged through the outlet 106, and the interior of the pressure chamber 101 was brought to atmospheric pressure. This caused gasification of the supercritical carbon dioxide on the silicon substrate that carried the substrate holder 102, and brought about a state in which supercritical drying occurred. The resist pattern on the silicon substrate obtained as a result of such supercritical drying was free from pattern collapse and had an adequate pattern shape.

[0038] In the working examples described above, ZEP-7000 and NEB-31 (electron-beam resists) were used as the resists, *n*-hexyl acetate and TMAH were used as the developing solutions, and 2-propanol, water, and ethanol were used as the rinsing solutions, but these are not the only possible options. Furthermore, the development and rinsing may be conducted inside or outside the pressure chamber 101.

[0039] In addition, the above description was given with reference to an example in which a resist pattern composed of polymeric material was used as the pattern to be dried, but it is also possible to apply this approach to the drying of patterns composed of silicon or compound semiconductors. Furthermore, carbon dioxide was used as the supercritical liquid in the above description, but this is not the only possible option, and CHF_3, NO_2, or another substance that has a critical point may also be used.

[0040]

[Effect of the Invention] As described above, the present invention entails placing an ultrasonic generator inside a container, and is therefore extremely effective in the sense that supercritical drying can be performed more rapidly as a result of removing the rinsing solution remaining on a pattern in a shorter time.

[Brief Description of the Drawings]

[Figure 1] A schematic cross section depicting the structure of a supercritical drying apparatus in accordance with an embodiment of the present invention

[Figure 2] A process diagram illustrating a process in which a rinsing solution and liquefied carbon dioxide are mixed by means of a the application of ultrasonic waves

[Figure 3] A schematic cross section depicting the structure of substrate holder 102

[Figure 4] A schematic cross section depicting the structure of a supercritical drying apparatus in accordance with another embodiment of the present invention

[Figure 5] A schematic cross section depicting the structure of a supercritical drying apparatus in accordance with yet another embodiment of the present invention

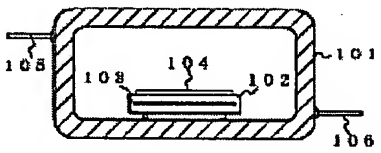
[Figure 6] A diagram illustrating the pattern collapse phenomenon

[Figure 7] A schematic cross section depicting the structure of a supercritical drying apparatus according to the prior art

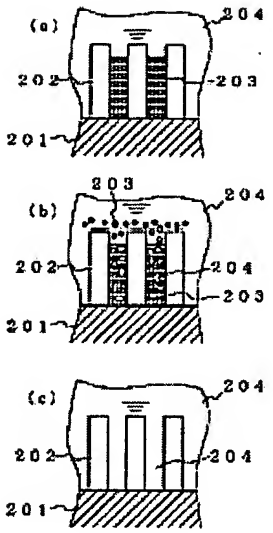
[Key]

101: pressure chamber (container), 102: substrate holder, 103: ultrasonic generator means, 104: substrate, 105: inlet, 106: outlet (discharge means)

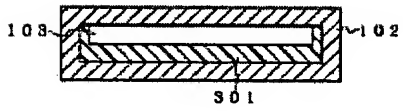
[Fig. 1]



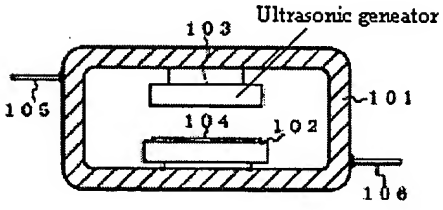
[Fig. 2]



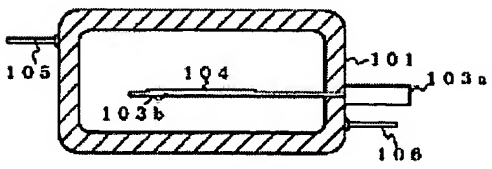
[Fig. 3]



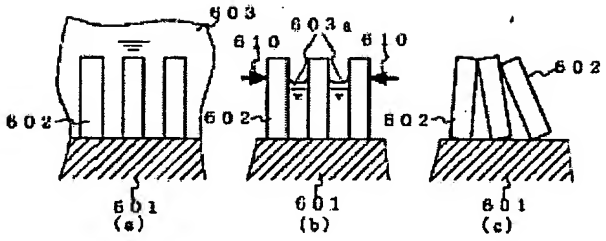
[Fig. 4]



[Fig. 5]



[Fig. 6]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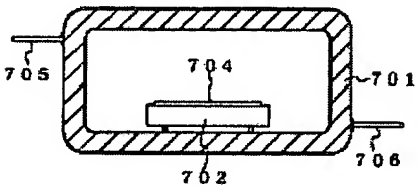
[Fig. 7]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